DOE Hydrogen Program

Characterization of PEMFC Membrane Durability

K. A. Mauritz
School of Polymers and High Performance Materials
University of Southern Mississippi
Hattiesburg, MS 39402

Project ID #
FCP 11

Overview

Timeline

- Project start date 6/1/06
- Project end date 5/31/08
- Percent complete 100%

Budget

- Total project funding
  - DOE share $495,000
  - Contractor share
- Funding received in FY07
  - $495,000
- Funding for FY08/09
  - $1,000,000

Barriers

- Barriers addressed
  - High chemical and mechanical degradation rate of Nafion®
  - Poor membrane dimensional stability against humidity change in fuel cells
  - High fuel crossover
  - Low proton conductivity

Partners

- Interactions / collaborations

Illinois Institute of Technology

Project lead: Dr. Vijay Ramani,

Dept. Chemical Engineering (unfunded)

Objectives

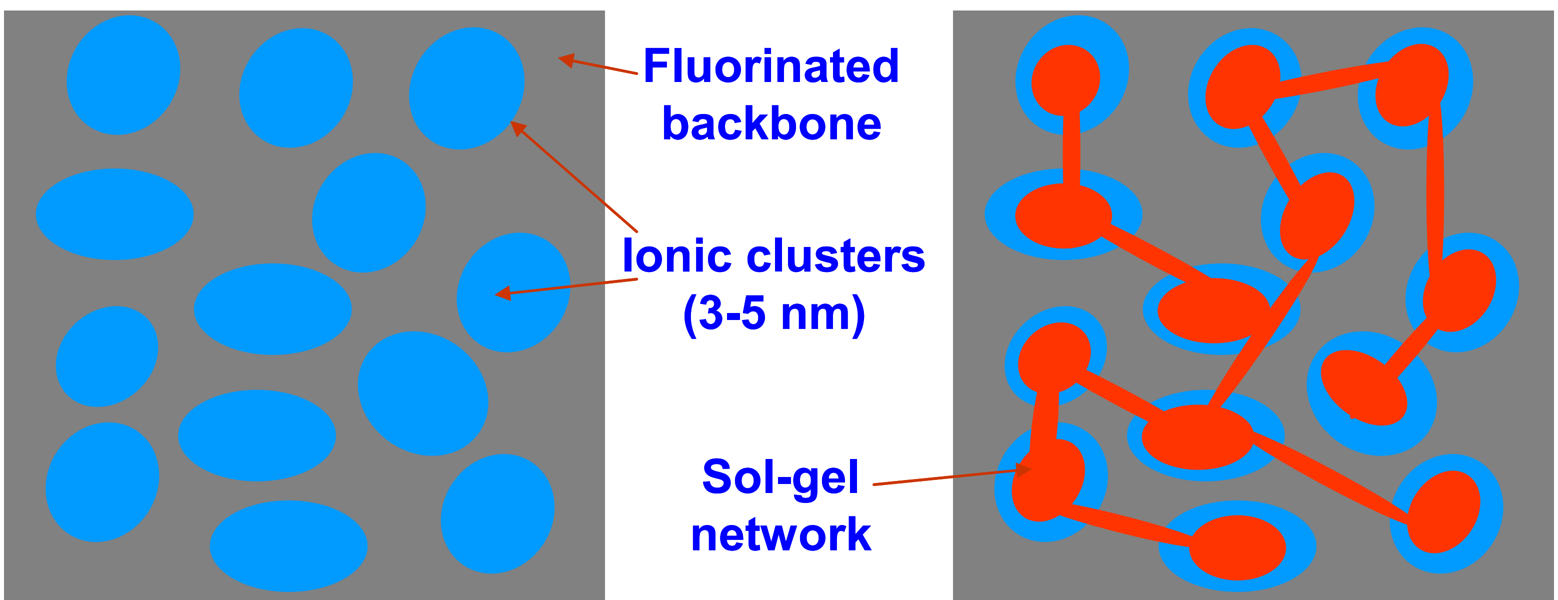
1. Evaluate chemical degradation via dielectric spectroscopy
2. Generate metal oxide quasi-network particles using *in situ* sol-gel processes for inorganic alkoxide monomers in Nafion® membranes.
3. Characterize structure/properties/FC performance of (2).
4. Enhance Nafion® chemical and mechanical durability via optimization of Nafion®/[metal oxide] nanocomposite membrane composition.

Milestones

Task Number	Project Milestones	Task Completion Date				Progress Notes
		Original Planned			Percent Complete	
1	Acquisition of Equipment	10/31/06			100%	Complete
2	Development of Characterization Methods	2/28/07			100%	Complete
3	Inorganic Modification of Membranes	6/30/07			100%	Complete
4	Membrane Durability Studies	10/31/07			100%	Complete

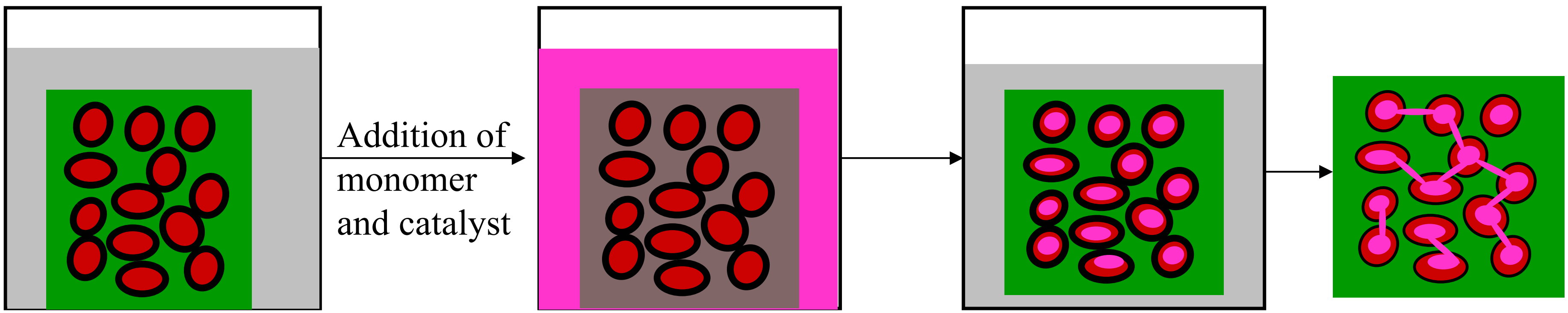
Approach

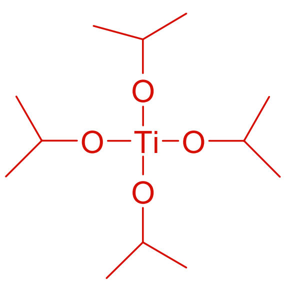
- Sol-gel processes to generate metal oxide nanoparticles in Nafion® sulfonic acid clusters causing mechanical reinforcement.
- Improve membrane modulus and dimensional stability under swell - de-swell.
- Reduce fuel crossover and minimize chemical degradation.
- Dielectric analysis of chemically degraded Nafion membranes



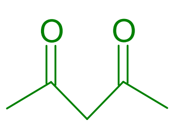
Domain targeted sol-gel reactions

Alcohol/water swelling | **Monomer diffusion and reaction** | **Alcohol wash to remove surface silicate** | **Oven drying under vacuum**

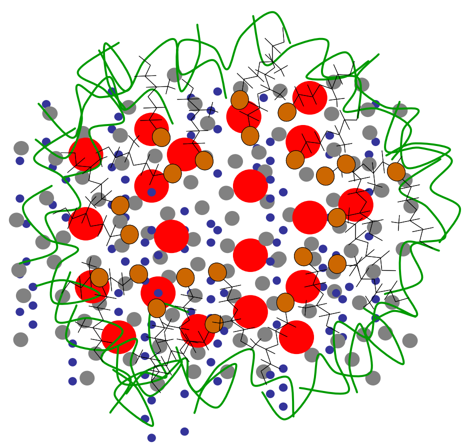




Titanium Isopropoxide



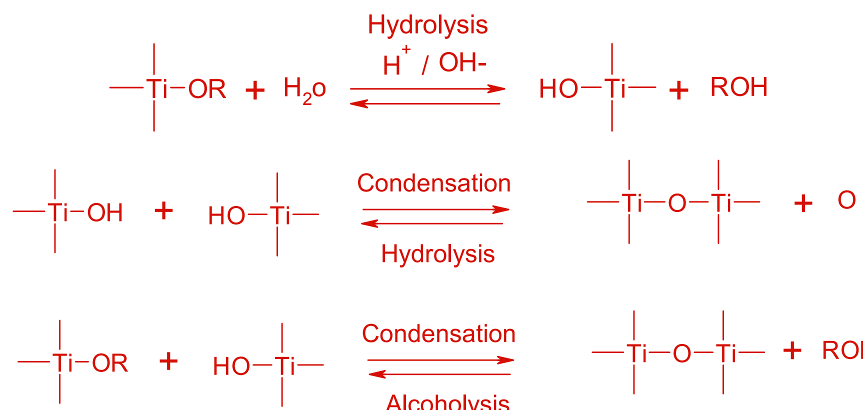
Acetyl Acetone

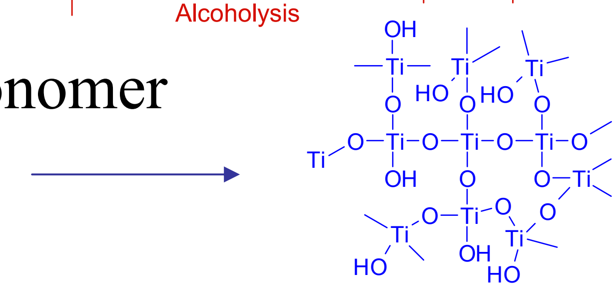


Sol-gel precursor monomer

Alcohol

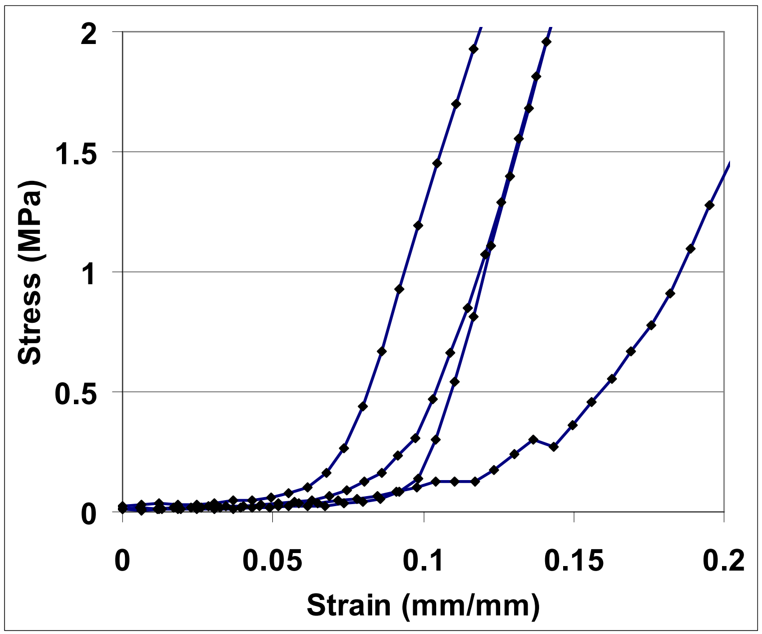
Water

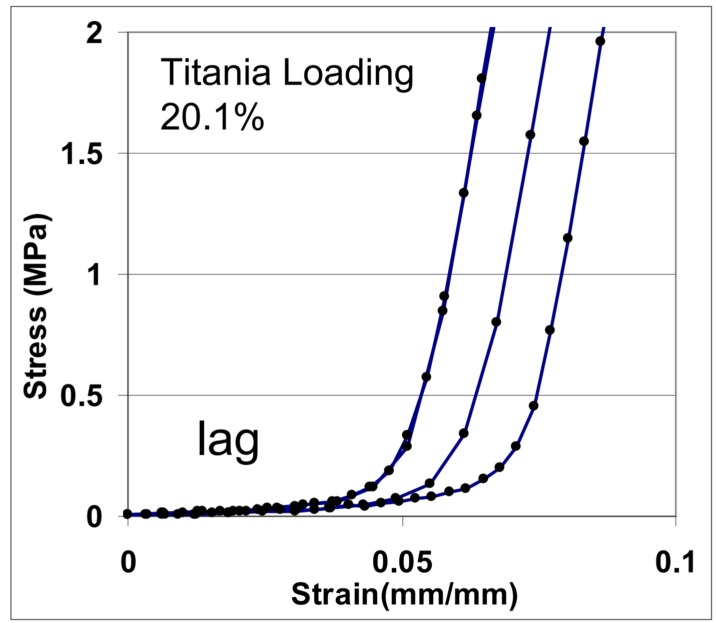




Early region of stress-strain curves at 80° C, 100% RH

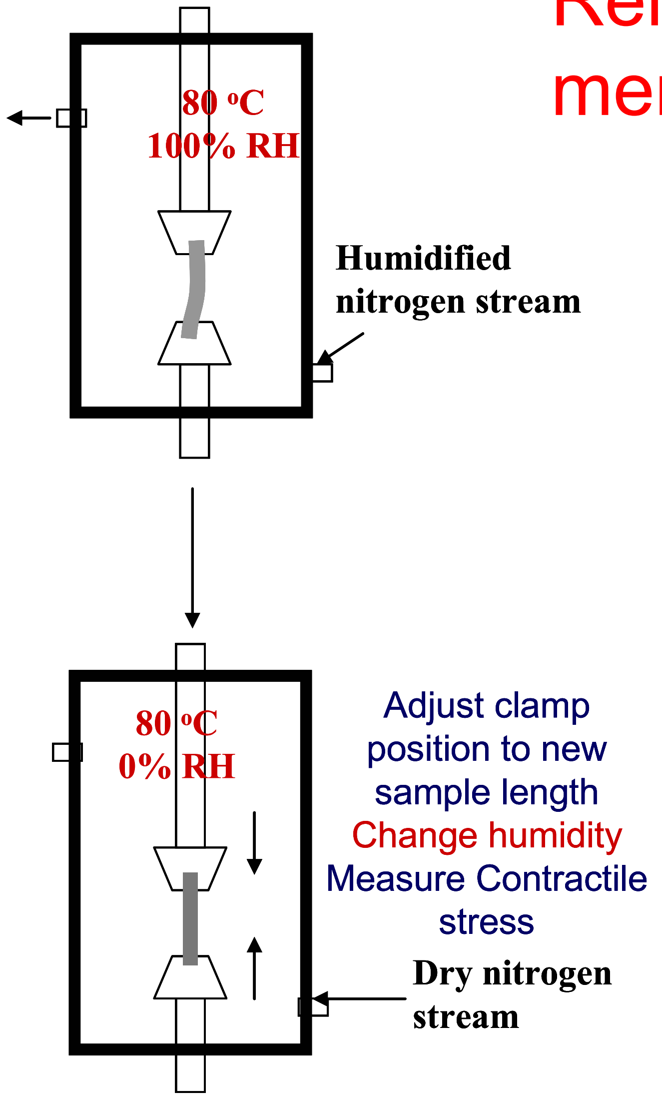
Titania reinforcement reduces swelling and improves membrane modulus and dimensional stability



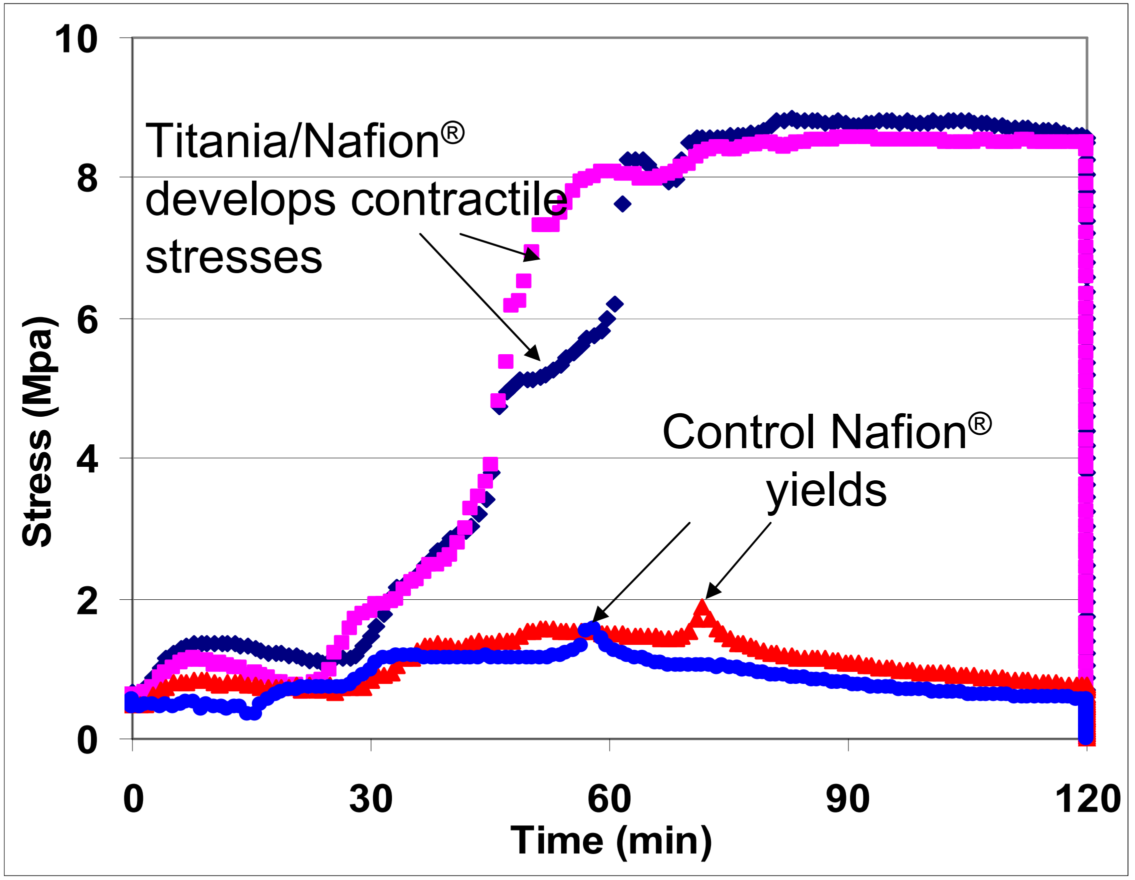


	Modulus (MPa)	Length increase due to humidity change (%)	Strain at break (mm/mm)	Stress at break (MPa)
Nafion®/Titania	120.4 $\pm$ 7.1	5.7 $\pm$ 1.0	3.1 $\pm$ 0.2	24.1 $\pm$ 1.68
Nafion®	36.2 $\pm$ 7.2	10.0 $\pm$ 3.2	4.1 $\pm$ 0.4	20.8 $\pm$ 3.2

Contractile Stress response to Humidity Drop from 100% to 0% at 80° C

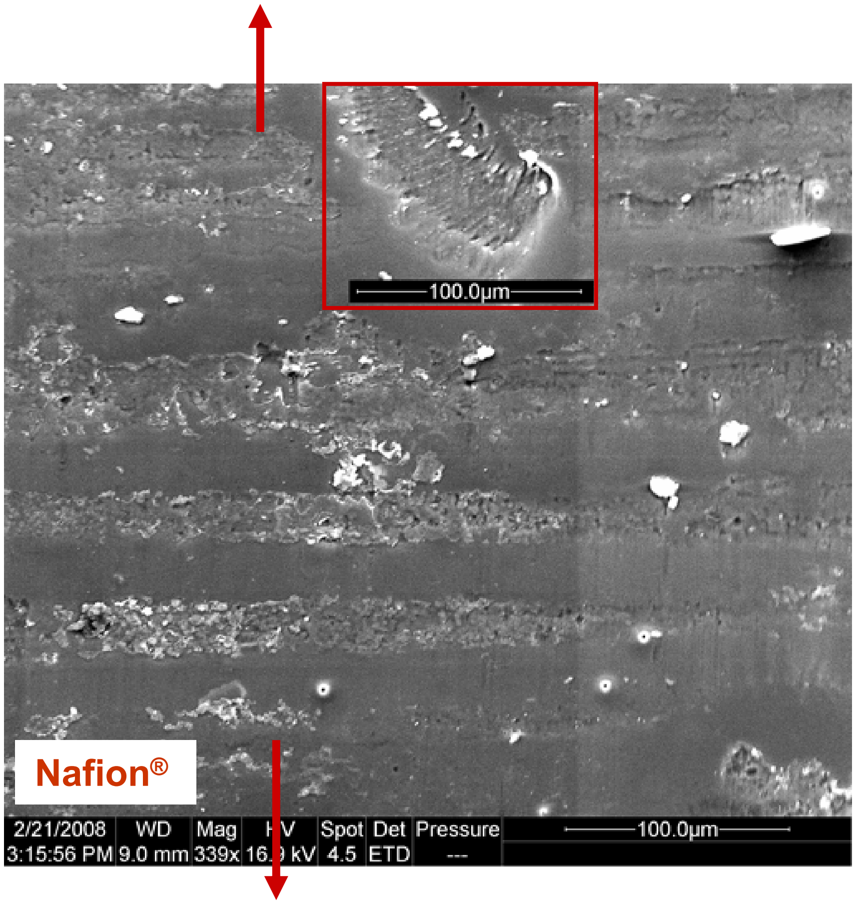


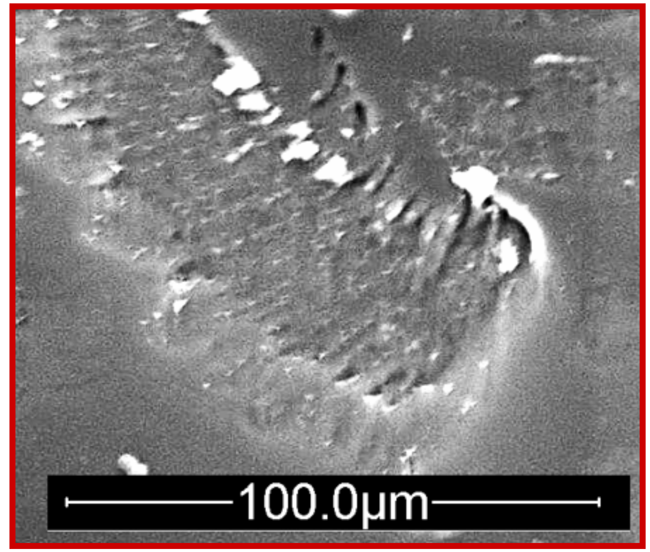
Reinforcement prevents membrane mechanical failure

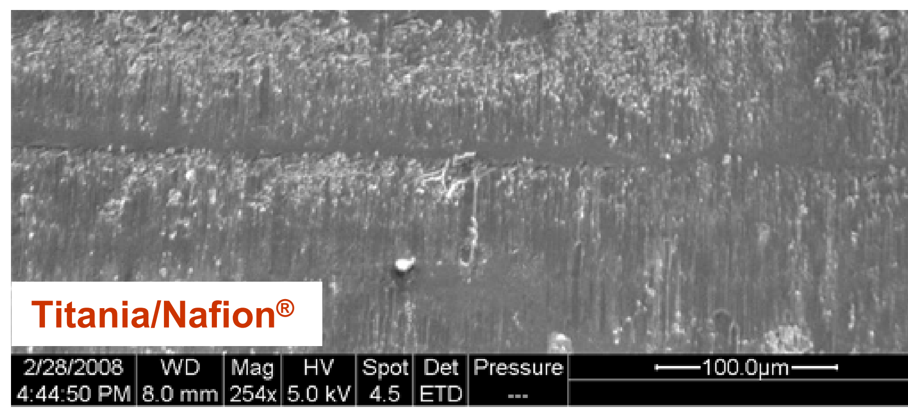


Unfilled and filled Nafion® after drying-contractile stress *vs.* time test

--- regions of damage by SEM



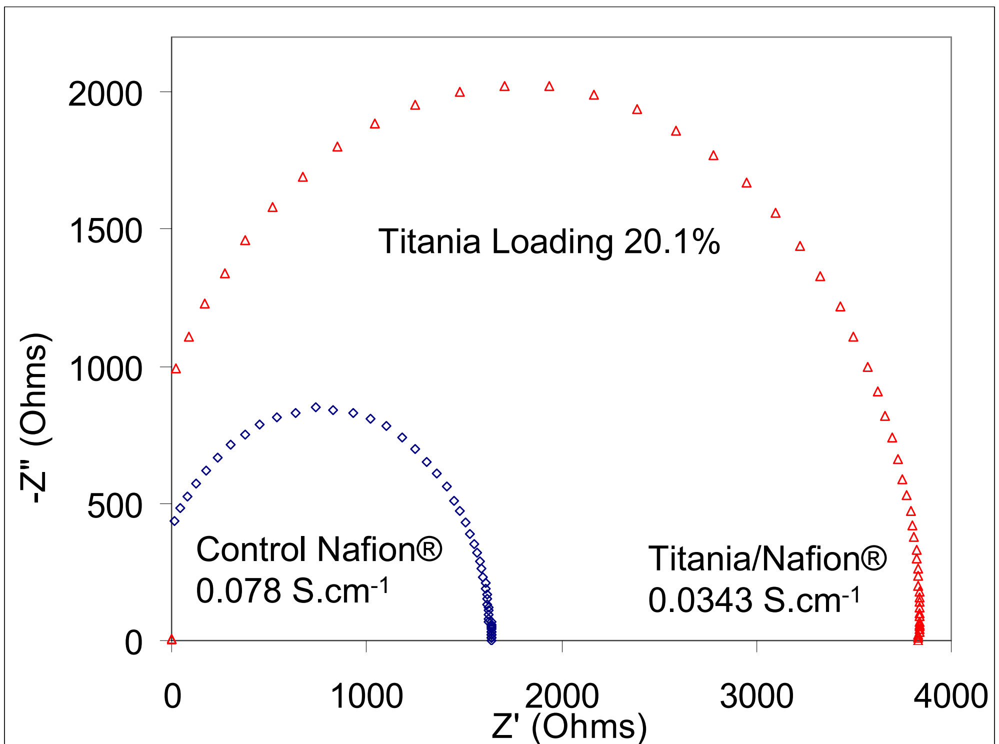




Arrow indicates direction of contractile stress exerted by sample during drying

Equivalent weight, water uptake, proton conductivity

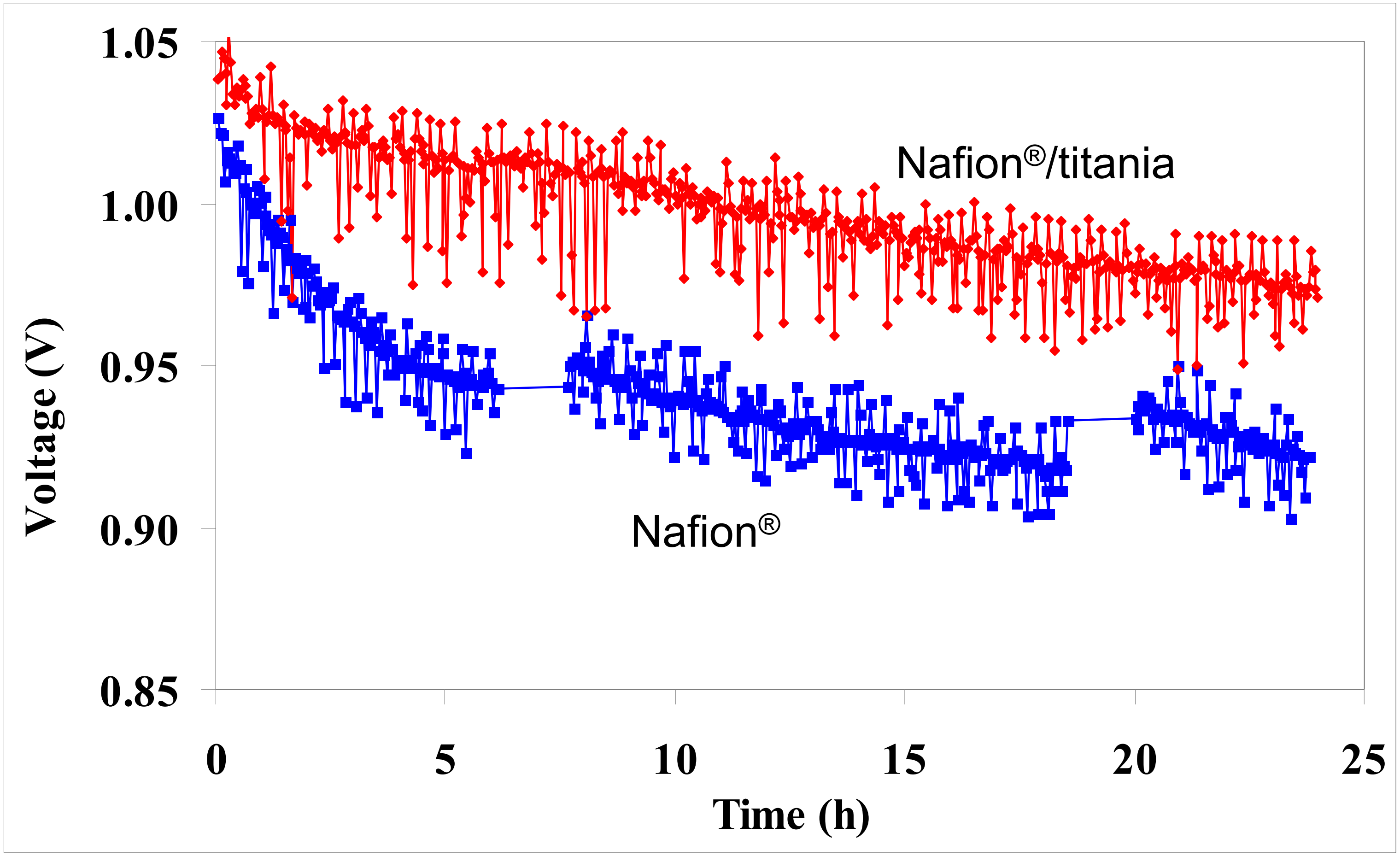
	Nafion®/titania	Nafion®
Water uptake (%)	13.6 $\pm$ 2.1	22.3 $\pm$ 2.0
Equivalent weight (g/mole)	1143 $\pm$ 20	1152 $\pm$ 37



- Acid functionality remains intact - reaction with, interference by titania quasi-networks.
- Water uptake reduced as volume inside clusters is occupied by inorganic network.
- Conductivity reduced due to restricted polymer chain mobility or/and increased tortuosity of proton conduction pathways.

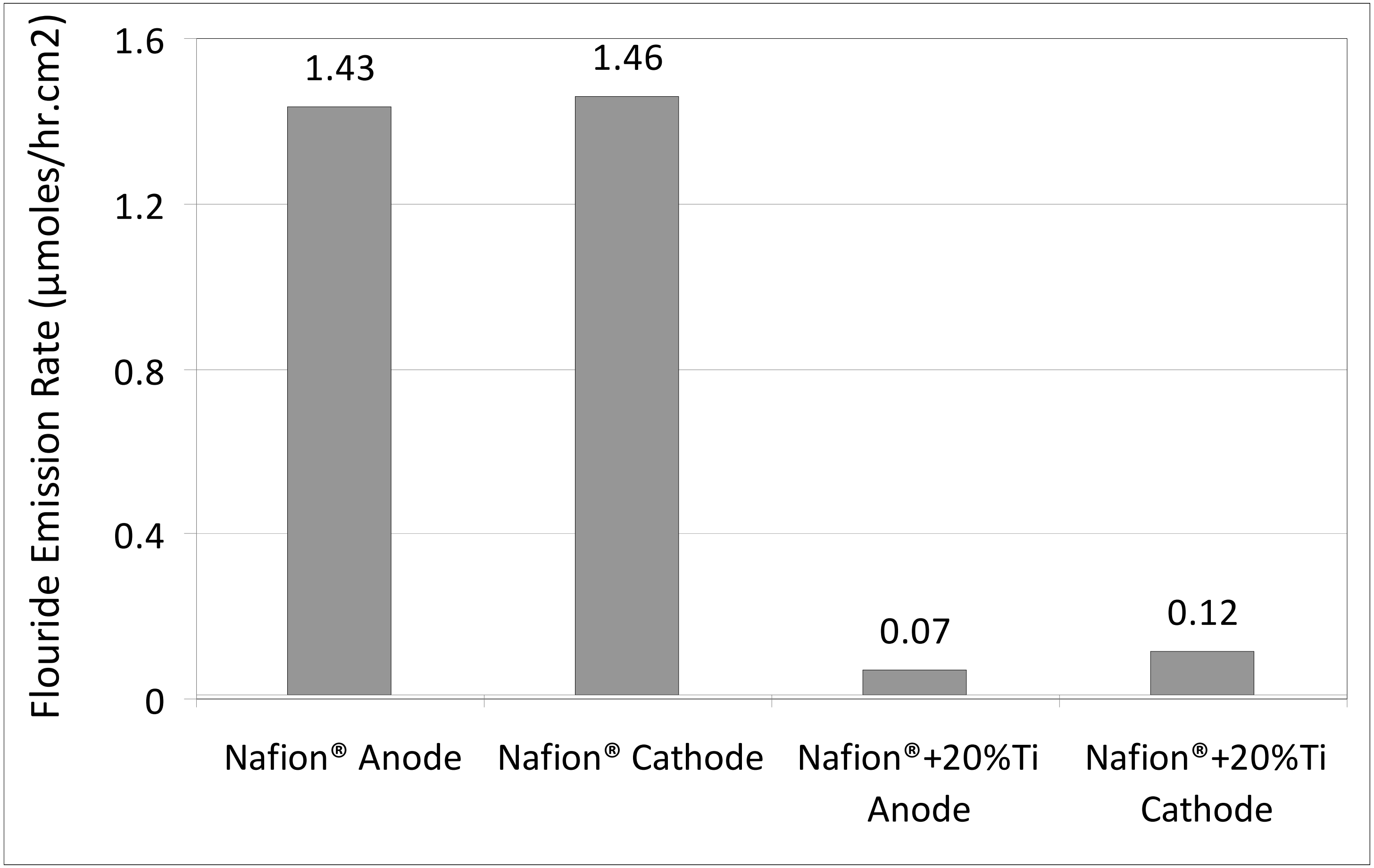
Accelerated OCV test at 100° C, 25% RH

Rate of voltage loss lower for Nafion®/titania relative to unmodified Nafion® membrane

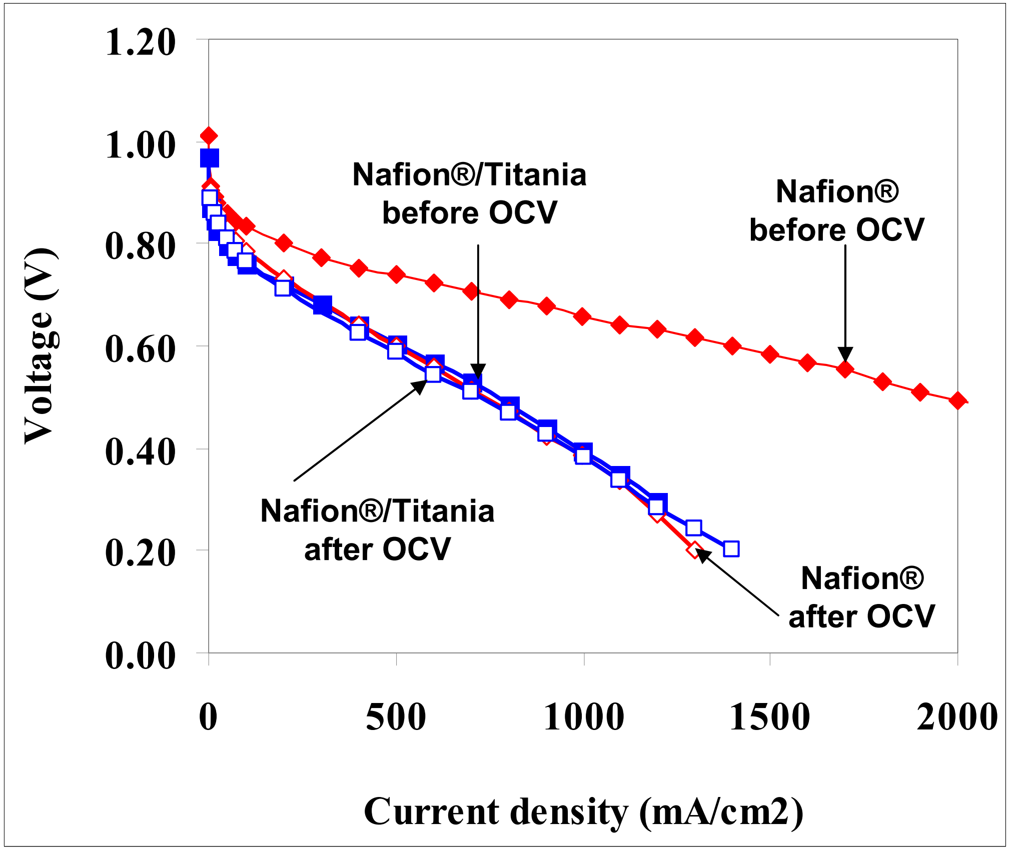


Fluoride emission rates

Nafion®/titania membrane has significantly lower chemical degradation - due to reduced fuel crossover

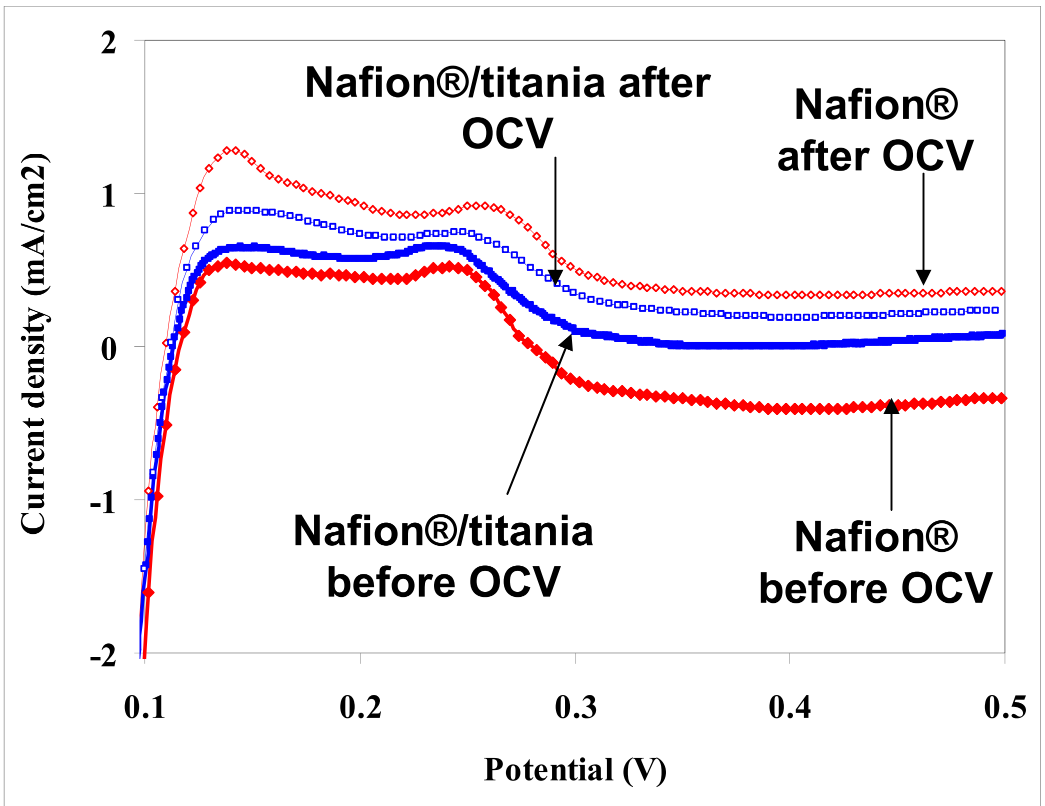


FC performance curves at 80° C, 75% RH before and after OCV



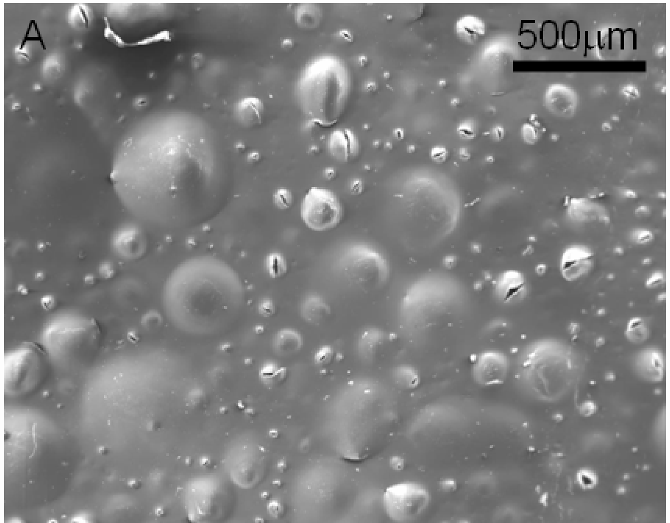
- Before OCV test, composite membrane has poor performance due to low water uptake and restricted polymer chain mobility.
- Nafion® membrane showed significant performance loss after OCV degradation test.
- Composite membrane performance is intact after OCV degradation test.
- Titania reinforcement minimized membrane degradation due to improved mechanical and gas barrier properties.

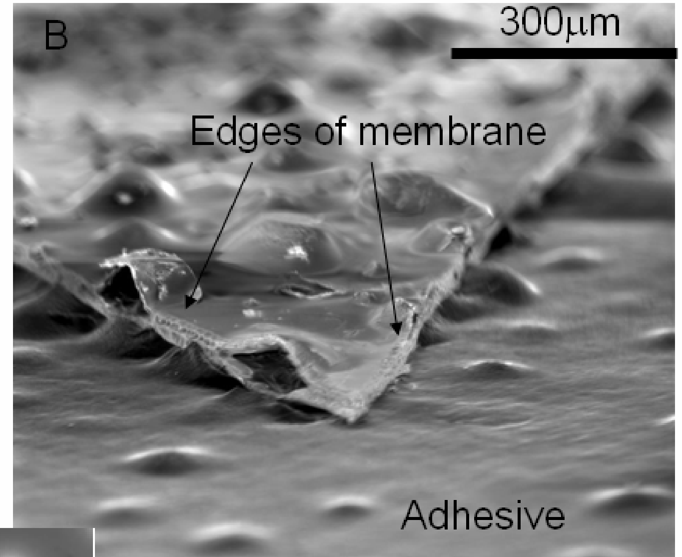
Hydrogen crossover current at ambient temperature before and after accelerated OCV test



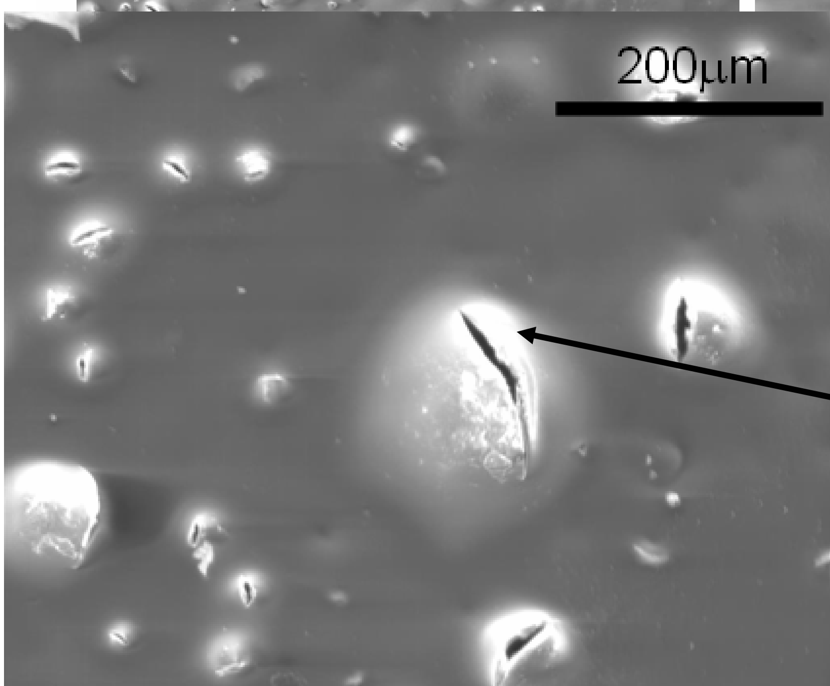
- Hydrogen crossover current more for composite membrane before OCV test
- After OCV test, increase in crossover current for Nafion® is higher than that of composite membrane

Accelerated Chemical Degradation





75h film exposure to Fenton's reagent



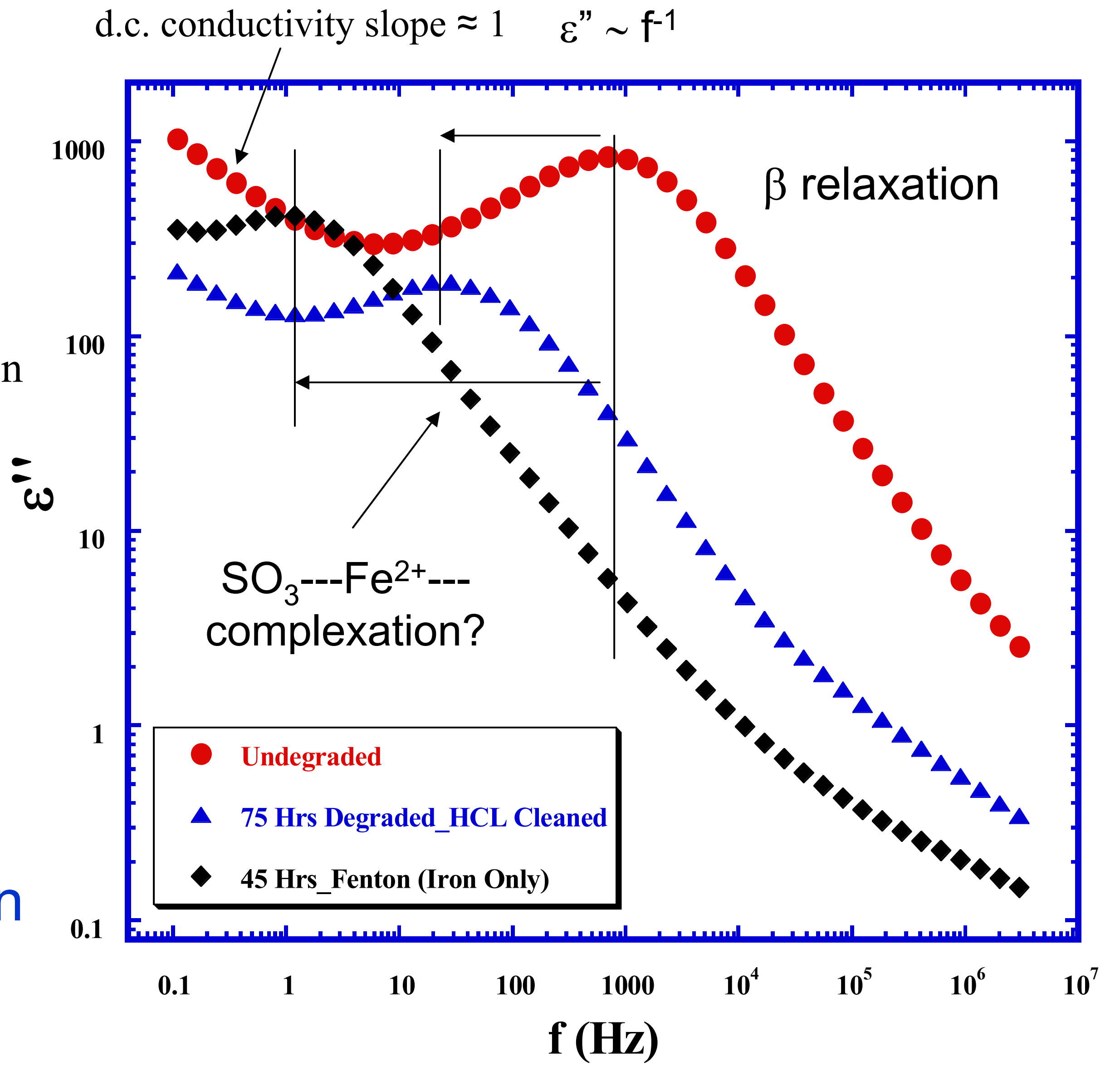
rupture crack

SEM: 75h film exposure to Fenton's reagent soln. (post-degradation cut)

Dielectric loss factor vs. f for degraded and non-degraded Nafion® at 60 °C

- f_{max} ↓ with degradation
- Relaxation time (τ) = $1/(2\pi f_{max})$ decreases
- Chain conformation dynamics, T_g – related motions
- Slower motions with degradation
  - a. Shift to higher MW
  - b. Complexation around SO_3H
- d.c. conductivity at low f.

Powerful tool to probe macromolecular motions affecting proton transport



Future Work

- In-depth studies of relationship between dielectric spectra and Nafion® macromolecular fragmentation.
- Optimization of inorganic oxide quasi-network structure so durability can be achieved without sacrificing membrane performance.
- Composite membrane MEAs will be subjected to various current and humidity cycles to test mechanical durability.
- Oxygen and hydrogen permeability under different temperature and humidity conditions will studied.
- Composite membranes for direct methanol fuel cell applications will be tested.

Summary

- Dielectric spectroscopy is a powerful tool for probing macromolecular motions in Nafion® and molecular weight degradation.
- Nafion® membrane *in situ* – grown titania nanoparticles improved barrier and mechanical properties and enhanced membrane durability by reducing physical and chemical degradation.
- Domain-targeted network incorporation pointed to a new route for prolonging the life of fuel cell membranes.